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**Japanese Patent Application JP 60 – 69133 A**

**Biaxially Oriented Polyester Film**

**Your Ref: 111403 - 01**

**For: Eastman Chemical Company**

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**SPECIFICATION****1. Title of the Invention**

Biaxially Oriented Polyester Film

**2. Claims**

(1) A poly-1,4-cyclohexylene dimethylene terephthalate film in which 1,4-cyclohexane dimethanol comprises 90 mol% or more of the glycol component and terephthalic acid comprises

80 mol% or more of the acid component, said film being biaxially oriented to yield an in-plane refractive index of 1.585 to 1.650 (including both longitudinal and transverse directions); a density of 1.220 to 1.250; a coefficient of temperature-induced expansion of 20 to 40 ( $\times 10^{-6}/^{\circ}\text{C}$ ); a coefficient of moisture-induced expansion of 3 to 8 ( $\times 10^{-6}/\% \text{ RH}$ ); an in-plane directional difference between the coefficients of temperature-induced expansion of within  $6 \times 10^{-6}/^{\circ}\text{C}$ ; and an in-plane directional difference between the coefficients of moisture-induced expansion of within  $4 \times 10^{-6}/\% \text{ RH}$ .

### **3. Detailed Description of the Invention**

#### **(Field of Industrial Utilization)**

The present invention relates to a biaxially oriented poly-1,4-cyclohexylene dimethylene terephthalate film. In further detail, the present invention relates to a film made from common biaxially oriented poly-1,4-cyclohexylene dimethylene terephthalate having the same longitudinal and transverse strength ratios, and having both a low coefficient of moisture-induced expansion coefficient and a small in-plane directional difference between the coefficients of temperature-induced expansion and moisture-induced expansion.

#### **(Prior Art)**

In conventional practice, biaxially oriented polyethylene terephthalate film is known as one type of common biaxially oriented film with a low coefficient of moisture-induced expansion. The characteristics of this film are well balanced, leading to its widespread use as an exceptional industrial material. However, it is not suited for flexible magnetic disks and other applications sensitive to moisture-induced dimensional changes.

#### **(Object of the Invention)**

It is an object of the present invention to provide a film that has the advantages and characteristics of biaxially drawn polyethylene terephthalate film, while having improved levels in terms of its long-term thermal degradation properties, coefficient of moisture-induced expansion, and the like; and to provide a film that has a small in-plane directional difference

between the coefficients of temperature-induced expansion and moisture-induced expansion, and that is preferably used as a base for flexible magnetic disks.

### **(Structure of the Invention)**

The inventors perfected the present invention as a result of performing diligent studies of various polymer characteristics.

Specifically, the present invention is a poly-1,4-cyclohexylene dimethylene terephthalate film in which 1,4-cyclohexane dimethanol comprises 90 mol% or more of the glycol component and terephthalic acid comprises 80 mol% or more of the acid component, said film being biaxially oriented to yield an in-plane refractive index of 1.585 to 1.650 (including both longitudinal and transverse directions); a density of 1.220 to 1.250; a coefficient of temperature-induced expansion of 20 to 40 ( $\times 10^{-6}/^{\circ}\text{C}$ ); a coefficient of moisture-induced expansion of 3 to 8 ( $\times 10^{-6}/\% \text{ RH}$ ); an in-plane directional difference between the coefficients of temperature-induced expansion of within  $6 \times 10^{-6}/^{\circ}\text{C}$ ; and an in-plane directional difference between the coefficients of moisture-induced expansion of within  $4 \times 10^{-6}/\% \text{ RH}$ .

The 1,4-cyclohexane dimethanol in the present invention can be produced, e.g., by means of a catalytic reduction of dimethyl terephthalate or terephthalic acid, but 1,4-cyclohexane dimethanol manufactured by means of any method can be used. There are no special limitations as to the ratio of the *cis* form and the *trans* form of the 1,4-cyclohexane dimethanol, but a preferred range for the *cis* form/*trans* form ratio is 4/6 to 0/10.

The poly-1,4-cyclohexylene dimethylene terephthalate of the present invention may be produced by means of any conventional method used for manufacturing polyesters. Examples of such methods include direct esterification of terephthalic acid and 1,4-cyclohexane dimethanol, and transesterification of dimethyl terephthalate and 1,4-cyclohexane dimethanol. The poly-1,4-cyclohexylene dimethylene terephthalate manufactured in this manner may be copolymerized with a third component in a small ratio. The poly-1,4-cyclohexylene dimethylene terephthalate may also contain, for example, a lubricant; a stabilizer such as phosphoric acid, phosphorous acid, or an ester thereof; or a delusterant such as titanium dioxide, silica fine particles, kaolin, calcium carbonate, or calcium phosphate.

It is essential for the biaxially drawn poly-1,4-cyclohexylene dimethylene terephthalate film of the present invention to have a refractive index in each direction at the film surface of 1.585 to 1.650, and preferably 1.590 to 1.630; a density of 1.220 to 1.250 g/cm, and preferably 1.224 to 1.240 g/cm; a coefficient of temperature-induced expansion of 20 to 40 ( $\times 10^{-6}/^{\circ}\text{C}$ ), and preferably 20 to 25 ( $\times 10^{-6}/^{\circ}\text{C}$ ); a coefficient of moisture-induced expansion of 3 to 8 ( $\times 10^{-6}/\% \text{ RH}$ ), and preferably 3 to 7 ( $\times 10^{-6}/\% \text{ RH}$ ); an in-plane directional difference between the coefficients of temperature-induced expansion of within  $6 \times 10^{-6}/^{\circ}\text{C}$ , preferably  $4 \times 10^{-6}/^{\circ}\text{C}$ ; and an in-plane directional difference between the coefficients of moisture-induced expansion of within  $4 \times 10^{-6}/\% \text{ RH}$ , and preferably  $3 \times 10^{-6}/\% \text{ RH}$ .

If the above-mentioned in-plane refractive index of the film is less than 1.585, the orientation of the molecular chains will be insufficient, and the film will lack the strength, particularly the Young's modulus, required in engineering applications. On the other hand, if the in-plane refractive index is greater than 1.65, the refractive index in a 90° direction to this surface will be 1.58 or less, and there will be an increase in the deviation of the molecular chain orientation. This deviation in the molecular chain orientation is undesirable since it is an object of the present invention to provide a film with a well-balanced orientation that may be used as a film for liquid crystal displays of flexible disks. An in-plane refractive index within a range of 1.590 to 1.630 is more preferable, and will lead to further improvements in orientation balance. The density of the film is 1.220 to 1.250 g/cm. If the density is lower than 1.220, crystallization will be inadequate, and it will not be possible to obtain the desired coefficient of moisture-induced expansion. A higher density is preferred, but making the density higher than 1.250 is problematic. The coefficient of temperature-induced thermal expansion of the film is 20 to 40 ( $\times 10^{-6}/^{\circ}\text{C}$ ), with 20 to 25 ( $\times 10^{-6}/^{\circ}\text{C}$ ) being preferred. The coefficient of temperature-induced expansion is generally better when smaller, but is preferably closer to the coefficient of temperature-induced expansion of the disk drive device when the film is used as a base for flexible magnetic disks in order to minimize head off-track relative to the magnetic disk. The coefficient of temperature-induced expansion of a disk drive device is readily set to approximately  $20 \times 10^{-6}/^{\circ}\text{C}$ , and therefore, a value close to  $20 \times 10^{-6}/^{\circ}\text{C}$  is preferably selected for the film; however, it is difficult to set this value to less than  $20 \times 10^{-6}/^{\circ}\text{C}$ . A smaller coefficient of moisture-induced expansion is better for most applications, but expansion associated with the

inherent moisture absorption of the material is inevitable, and it is therefore difficult to set the coefficient of moisture-induced expansion to less than  $3 \times 10^{-6}/\% \text{ RH}$ . However, as long as this coefficient is  $8 \times 10^{-6}/\% \text{ RH}$  or smaller, the film will be of use because it will demonstrate evident improvement over the  $11 \times 10^{-6}/\% \text{ RH}$  level of conventional polyethylene terephthalate. The in-plane directional difference between the coefficients of temperature-induced expansion is  $6 \times 10^{-6}/^{\circ}\text{C}$  or less, and preferably  $4 \times 10^{-6}/^{\circ}\text{C}$  or less, in order to minimize off-tracking, as mentioned in the foregoing. A smaller in-plane directional difference in the coefficients of moisture-induced expansion is also preferred in order to minimize off-tracking, with the difference being  $8 \times 10^{-6}/\% \text{ RH}$  or less, and preferably  $7 \times 10^{-6}/\% \text{ RH}$ .

The methods by which the values specified above are obtained will now be described.

Terephthalic acid comprises 80 mol% or more of the acid component of the poly-1,4-cyclohexylene dimethylene terephthalate used in the present invention. If the terephthalic acid component is present in a smaller amount, the polymer crystallinity will be inadequate, and it will be impossible to satisfy the above-mentioned ranges for the refractive index, density, and coefficients of temperature-induced expansion and moisture-induced expansion. Isophthalic acid, oxalic acid, succinic acid, adipic acid, 2,6-naphthalenedicarboxylic acid, and the like may be used as a third component within a range of 20 mol% or less. Moreover, 1,4-cyclohexane dimethanol comprises 90 mol% or more of the glycol component. At a lower ratio, the polymer crystallinity will decrease, and the above-mentioned values; in particular the density, will not come within the preferred ranges. The refractive index will also decrease, which is not preferable. Ethylene glycol, propylene glycol, 1,4-butanediol, and the like can be used as a third component as long as the ratio is 10 mol% or less. The above-mentioned 1,4-cyclohexane dimethanol exists in *cis*- and *trans*-forms, and although the mixture ratio will not have a large effect, slight changes in the physical characteristics may be observed with certain ratios. As previously mentioned, the ideal range of the above-mentioned characteristics may be obtained as long as the *cis/trans* ratio is within a range of 4/6 to 0/10.

The film manufacturing conditions will now be described. The polymer chips may be dried at approximately  $170^{\circ}\text{C}$  for approximately 3 hours, but drying is not limited to these conditions. A conventional extruder may be used, but preferably with some provision made

particularly for improving the extrusion precision; e.g., additionally using a metering pump, or employing a pressure control technique. The temperature of the molten poly-1,4-cyclohexylene dimethylene terephthalate will change according to the above-mentioned polymer composition, and should therefore be selected as needed in accordance therewith. The temperature range that is usually selected with the above-mentioned polymer composition is 295 to 315°C. A temperature of 10 to 60°C is appropriate for the casting drum, but quenching is preferably performed at a temperature approximating that of the poly-1,4-cyclohexylene dimethylene terephthalate homopolymer, in which case a surface temperature of 20 to 40°C is suitable. The stretching temperature is usually 80 to 140°C. If a lower stretching temperature is used, stretching irregularities will develop, while if a higher temperature is used, the stretching effect will tend to deteriorate. The stretching temperature is preferably selected from within a range of 100 to 120°C in order for the above-mentioned values for the physical characteristics to be readily obtained. The draw ratio in the longitudinal direction is selected from 300 to 500%, and preferably 330 to 430%, while the draw ratio in the transverse direction is selected from 300 to 500%, and preferably 350 to 450%. A draw ratio of less than specified above will be undesirable because the refractive index will be smaller than the above-mentioned value, while a draw ratio exceeding this range will be undesirable because the film will frequently rupture during manufacture. Moreover, the coefficient of moisture-induced expansion will be unexpectedly high even if a film is obtained, and satisfactory results will not be obtained.

The stretching method can be a conventional method. For instance, longitudinal stretching can be accomplished if stretching is performed under heating between two rolls with different peripheral speeds, and transverse stretching can be accomplished if both ends of the film are supported with clips while the distance between the clips is increased under heating. The refractive index, density, and coefficients of temperature-induced expansion and moisture-induced expansion of the present invention are obtained by means of heat-setting the resulting biaxially oriented film for 1 to 100 seconds at 150 to 260°C, and preferably at 180 to 250°C. If the film is manufactured according to conventional longitudinal-transverse stretching methods, the in-plane directional difference between the coefficients of temperature-induced expansion and the coefficients of moisture-induced expansion near the center along the width direction of the film will come within the ranges of the present invention. However, the quantitative



percentage of width included will vary according to the film manufacturing conditions and polymer composition. Usually 10 to 70% of total width will come within the ranges of the present invention. On the other hand, the regions near both ends of the film along the width direction have a large in-plane directional difference between the coefficients of temperature-induced expansion and the coefficients of moisture-induced expansion, and this difference does not usually come within the range of the present invention. The underlying explanation therefor is a bowing phenomenon that occurs when the film is heat-set in a tenter. A preferred method for reducing the in-plane directional difference between the coefficients of temperature-induced expansion and the coefficients of moisture-induced expansion at any region along the direction of width of the film involves heat-setting the film at a temperature of 120 to 180°C, winding the heat-set film, and then further heat-setting the film at a temperature of 180 to 250°C while taking off the film and supporting both ends thereof with clips. However, heat setting is not limited to this method. When heat treatment is performed two or more times in this manner using different heat treatment directions, the effect of the above-mentioned bowing can be eliminated by means of selecting the appropriate temperature conditions. As a result, the difference in the in-plane refractive index and in temperature-induced and moisture-induced expansion can be reduced over the entire film, thereby enabling an increase in the proportion of final products conforming to the present invention.

The optimal heat-setting conditions will vary with the composition of the above-mentioned polymer, and it is therefore essential to suitably select the conditions to be adopted. For instance, heat setting is ideally performed at 230 to 240°C for 20 to 40 seconds when the polymer has a composition that comprises 87 mol% of terephthalic acid and 13 mol% of isophthalic acid as the acid component, and 100% 1,4-cyclohexane dimethanol as the glycol component.

The biaxially oriented film of the present invention may be obtained at an appropriate thickness according to its use, but the thickness is selected from a range of 2 to 500  $\mu\text{-m}$ , normally 12 to 125  $\mu\text{-m}$ , and 50 to 100  $\mu\text{-m}$  when the film is used as a base for flexible disks.

The methods for measuring the values of the physical characteristics of the present invention are as follows.

(1) Refractive index: Measured with an Abbe refractometer.

(2) Density: Measured with a normal heptane-carbon tetrachloride density gradient tube.

(3) Coefficient of temperature-induced expansion: Measured by means of placing a constant-load elongation tester made by Nippon Jido Seigyo Co., Ltd. (model TTL2) in a thermo-humidistat. The measurement sample was heat-treated under pre-determined conditions (for example, 70°C for 30 minutes); affixed to the tester; and the coefficient of temperature-induced expansion was measured by means of determining the dimensional change between a temperature of 20°C and 60% RH and a temperature of 40°C and 60% RH. The original sample length was 505 mm, and the sample width was 1/4 inch. The load applied during the measurements was a constant 5 g per 1/4 inch width. If a long sample could not be obtained, the coefficient could also be measured using a TM-3000 thermomechanical analyzer (ULVAC-Riko, Inc.). The TM-3000 was used to find the difference between the maximum and the minimum coefficients of temperature-induced expansion. The dimensions of the sample were 15 mm (length) and 5 mm (width), and the difference was found by means of determining the dimensional change between a temperature of 10°C and 0% RH and a temperature of 40°C and 0% RH.

(4) Coefficient of moisture-induced expansion: Measured using the same constant-load elongation tester manufactured by Nippon Jido Seigyo Co., Ltd. as was used to determine the coefficient of temperature-induced expansion. A sample that had been pre-treated under a temperature of 40°C and humidity of 90% RH was affixed to the tester, and the coefficient of moisture-induced expansion was obtained by means of determining the dimensional change between a temperature of 20°C and 30% RH and 20°C and 70% RH. If a long sample could not be obtained, the coefficient was measured under the above-mentioned conditions by means of placing a thermomechanical analyzer (ULVAC-Riko, Inc.) inside a thermo-humidistat in the same manner employed when measuring the coefficient of temperature-induced expansion and measuring the coefficient.

(5) In-plane directional difference between the temperature-induced expansion coefficients and the moisture-induced expansion coefficients: The coefficient was measured

every 15° or 30° in each direction by means of the method described in (3) or (4) above, and the difference between the maximum and minimum values (i.e., maximum value – minimum value) was determined.

### **(Working Examples)**

The present invention will now be described in detail with reference to working examples.

#### **Working Example 1**

Using 85 mol% of terephthalic acid and 15 mol% of isophthalic acid as the dibasic acid component, and 100% [sic] of 1,4-cyclohexane dimethanol as the glycol component, 0.05 mol% of titanium oxide (per acid component) was added as a catalyst, and 0.5 wt% kaolin clay with an average particle diameter of 0.6 microns was added as a lubricant. This mixture was introduced into an autoclave, with transesterification and then polycondensation being performed under heating and stirring in order to obtain poly-1,4-cyclohexylene dimethylene terephthalate.

This polyester was melt-extruded at 300°C, then cooled on a quenching drum kept at 40°C to obtain an unstretched film with a thickness of 1,000  $\mu$ . This unstretched film was pre-heated as a result of being brought into contact with a metal roll adjusted to 90°C, then stretched 360% in the longitudinal direction between rolls with different peripheral speeds while being exposed to an infrared ray heater (surface temperature of 1,000°C). Next, the longitudinally stretched film was transversely drawn 370% at 115°C in a tenter, whereupon the resulting biaxially stretched film was heat-set at 140°C, and taken up with both ends supported with the help of clips. The film was then rolled out and again heat-set at 235°C with both ends of the film supported, to obtain a product with a thickness of 75  $\mu$ . The values for the physical characteristics of this film are shown in Table 1.

#### **Working Example 2**

A biaxially oriented film with a thickness of 75  $\mu$  was obtained in the same manner as described in Working Example 1, with the exception that the dibasic acid component was 100 mol% of terephthalic acid, the melting temperature was 310°C, the quenching drum

temperature was 20°C, the pre-heating temperature was 80°C, the initial heat-set temperature was 180°C, and the further heat-set temperature was 250°C. The values for the physical characteristics of this film are shown in Table 1.

### **Working Example 3**

A biaxially oriented film with a thickness of 75  $\mu$  was obtained in the same manner as described in Working Example 1, with the exception that the initial heat setting was performed at 235°C, but no further heat-setting was performed. The other conditions were the same as described in Working Example 1. The values for the physical characteristics of this film are shown in Table 1.

### **Comparative Example 1**

Polyethylene terephthalate was polymerized by means of a conventional method. A biaxially oriented film with a thickness of 75  $\mu$  was obtained as described in Working Example 1, with the exception that the film was manufactured with a melting temperature of 290°C, a quenching drum temperature of 20°C, a longitudinal stretching pre-heating temperature of 80°C, a transverse stretching temperature of 105°C, and a further heat-setting temperature of 225°C. The values for the physical characteristics of this film are shown in Table 1.

### **Comparative Example 2**

A biaxially oriented film with a thickness of 75  $\mu$  was obtained in a manner identical to the one as described in Working Example 2, with the exception that the draw ratio was 430% longitudinally and 350% transversely. The values for the physical characteristics of this film are shown in Table 1.

The central regions of the films produced as described in Working Examples 1, 2, and 3 satisfied the target values of the present invention.

Table 1

	Polymer composition (mol%)	Refractive index of film in each direction		Density (g/cm <sup>3</sup> )	$\alpha$ ( $\times 10^{-6}/^{\circ}\text{C}$ )		$\alpha h$ ( $\times 10^{-6}/\% \text{ RH}$ )		$\Delta\alpha$		$\Delta\alpha h$	
		central region of film	ends		central region of film	ends	central region of film	ends	central region of film	ends	central region of film	ends
WE1	Terephthalic acid 85 Isophthalic acid 15 1,4-Cyclohexane dimethanol 100	1.599 – 1.603	1.597 – 1.605	1.228	34 – 38	33 – 39	6	6	4	6	0	0
WE2	Poly-1,4-cyclohexylene dimethylene terephthalate	1.620 – 1.625	1.620 – 1.625	1.230	24 – 26	24 – 26	4	4	2	2	0	0
WE3	Terephthalic acid 85 Isophthalic acid 15 1,4-Cyclohexane dimethanol 100	1.599 – 1.603	1.580 – 1.625	1.228	34 – 38	25 – 47	6	5 – 8	1	3	0	3
CE1	Polyethylene terephthalate	1.658 – 1.660	1.657 – 1.661	1.396	14 – 15	13 – 16	9	8 – 11	4	22	0	3
CE2	Poly-1,4-cyclohexylene dimethylene terephthalate	1.580 – 1.655	1.580 – 1.655	1.230	15 – 42	14 – 45	2 – 6	1 – 9	27	31	4	8

Notes:  $\alpha$ : coefficient of temperature-induced expansion  
 $\alpha h$ : coefficient of moisture-induced expansion  
 $\Delta\alpha$ :  $\alpha_{\text{max}} - \alpha_{\text{min}}$  with respect to  $\alpha$  in both directions  
 $\Delta\alpha h$ :  $\alpha h_{\text{max}} - \alpha h_{\text{min}}$  with respect to  $\alpha h$  in both directions  
 ["WE" = working example; "CE" = comparative example]

### **(Effect of the Invention)**

The biaxially oriented film of the present invention is preferably used as a base for flexible magnetic disks, because its coefficient of moisture-induced expansion is smaller than that of polyethylene terephthalate film; therefore, the off-tracking of the head in relation to the magnetic disk is minimized, and a high recording density is obtained. Although the coefficient of temperature-induced expansion is relatively large, this is not a major drawback because the coefficient of temperature-induced expansion is close to that of the drive device and comes within a range that can match that of the disk. Moreover, the in-plane directional difference between the coefficients of temperature-induced expansion is small; therefore, the film can be successfully adapted even to applications in which off-tracking is reduced by means of a servo tracking mechanism. On the other hand, the film of the present invention has a small in-plane directional difference between refractive indices, and is suitably used for protective covers and transparent conductor films for liquid crystal displays.